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Analysis of explosives and propellants by 14 MeV neutron activation analysis technique

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Abstract : Concentrations of nitrogen, oxygen and chlorine in a few samples of high explosives and propellants are estimated by 14 MeV neutron activation analysis technique. Samples were irradiated with 14 MeV neutrons of flux$\sim 10^8$n/cm^2/sec and the gamma-ray activities, due to ^{13}N, ^{16}N and ^{37}S produced respectively through, nitrogen, oxygen and chlorine, were recorded by a HPGe detector and analysed to obtain values of concentrations. The method is found to be safe and convenient for analysis of explosive and propellant. The results of analysis are in good agreement with the theoretically evaluated values and are useful as a guide line to decide suitability of explosive and propellant for practical applications.

Keywords : 14 MeV neutrons, monitor, gamma rays, activation analysis.

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1. Introduction

Nitrogen, oxygen, and chlorine are the elements commonly present in almost all kinds of explosives and propellants. The nitrogen is invariably present in the explosives in the form of nitrate, azide and fulminate groups which are responsible for their explosive character. Amongst these groups, presence of the nitro group is desirable to achieve good explosive power (Services Text Book 1976). Oxygen, which is bonded to nitrogen in different functional groups, is utilized by the explosive while undergoing a rapid and exothermic decomposition resulting in detonation. Every explosive contains a definite N/O ratio and therefore, it is desirable to know the total nitrogen and oxygen contents in an explosive for accessing its power. The knowledge of the N/O ratio can also help to identify an unknown explosive. Similarly by knowing net amount of chlorine, one can directly estimate percentage of ammonium perchlorate in given samples of explosive and propellant.

Propellants, specially double base and CMDB type, on long storage have tendency to undergo slow decomposition with evolution of nitrogen in the form of its oxides, thereby adversely affecting their compositions and subsequently the ballistic and burning properties. It may be therefore, necessary to monitor their compositions before actual application. Stability behaviour of a propellant is normally studied by a method known as Abel's heat test (Service text book of explosives 1954). However, this method does not provide information about the amount of nitrogen or oxygen evolved from the sample due to its decomposition, when heated for the test purpose in the temperature range 71.6 to 82.2°C.

There are various destructive (Chemical) and non-destructive methods reported in literature to estimate nitrogen content of nitrocellulose, explosives and propellants (Yinon *et al* 1981, Rigdon *et al* 1983, Daros *et al* 1987, Bibby and Champion 1974, Malone *et al* 1976). Chemical and other methods are time consuming and need lot of sample handling which is undesirable. In the present study, 14 MeV neutron activation analysis technique is used to estimate concentrations of nitrogen, oxygen and chlorine in a few samples of high explosives and propellants. The experimentally determined values of the concentrations of these elements are in good agreement with the values theoretically estimated either from the chemical formula or the process of formation of the explosives and propellants. In addition to this, amount of nitrogen lost from the sample of a triple base propellant due to its decomposition on heating at 71.6°C was estimated.

2. Experimental method

The 14 MeV neutron generator (Joglekar *et al* 1978) of the Department of Physics, University of Poona, was used for this work. The different conventional explosives were synthesized in the laboratory by following the known procedure. Different types of propellant and explosive samples were supplied by the Institute of Armament Technology, Pune, for the present work, the details of which are given in Table 1.

All the samples of explosives and propellants were analysed by comparator method (Bhoraskar *et al* 1976). Samples for analysis were prepared by mixing uniformly a known quantity of explosive or propellant with a monitor powder. For ease of handling, each type of mixture was packed separately in polyethylene vials. A fast pneumatic transfer system was used to carry vial from the detector end to the irradiation head and back. All the samples were irradiated with 14 MeV neutrons, flux $\sim 10^8$ n/cm^2/sec, for a period depending on the half life of the radioactive isotope of interest. The induced gamma-ray activities were recorded on a HPGe detector (30% efficiency and FWHM ~3 KeV) coupled to a

4096 channel analyser, and the data was analysed using a computer program. All the standard corrections were made, while calculating area under a photopeak and weight of an element in the sample.

Table 1. Concentrations of nitrogen and oxygen in a few samples of propellants and explosives.

Samples propellant/ explosive	Nitrogen		Oxygen	
	Calculated %	Experimental %	Calculated %	Experimental %
WM Cordite (a)	13.5	13.0	56.0	58.0
SC (Solventleas Cordite) (b)	15.6	17.0	56.2	58.0
Triple base (c)	32.95	31.0	49.9	48.0
Ammonium perchlorate	11.91	10.0	54.4	56.0
TNT	18.5	17.0	42.2	40.0
RDX	37.8	36.0	43.2	42.0
Tetryl	24.3	26.0	44.6	46.0

(a) Compositions : NC, 65% (N, 12.2%) ; NG, 29.5% Mineral jelly 3.5%.

(b) Compositions : NC, 49.5% (N, 12.2%) ; NG, 41.5%, Carbamite, 9%.

(c) Compositions : NC, 27% (N, 13.2%), NG, 32%, Picrite, 40% Carbamite, 1% and K_2SO_4, 1%.

2.1. *Estimation of nitrogen :*

For estimation of nitrogen, pure (99.9%) aluminium powder was used as a monitor. Each sample was irradiated for ten minutes and the induced gamma-ray activities due to ^{13}N and ^{27}Mg were measured for ten minutes. ^{14}N on interaction with 14 MeV neutron produces ^{13}N through the following nuclear reaction.

$$^{14}N\,(n, 2n)^{13}N\ ;\ \sigma = 5.7\ mb \qquad (1)$$

^{13}N decays with half life period ($T_{1/2}$) of 9.96 minutes, by emitting positrons, which on annihilation produce gamma-rays of energy 0.511 MeV. Simultaneously the ^{27}Al in the mixture produces ^{27}Mg through the following nuclear reaction

$$^{27}Al\,(n,p)^{27}Mg\ ;\ \sigma = 81\ mb \qquad (2)$$

^{27}Mg, with half life ($T_{1/2}$) of 9.46 minutes, emits in its decay process gamma-rays of energies 0.84 MeV (70%) and 1.01 MeV (30%). Weight of nitrogen in the test sample was estimated using the following formula,

$$W_N/W_{Al} = KC_N/C_{Al} \qquad (3)$$

where W_N is the weight of nitrogen in the test sample, W_{Al} is the weight of aluminium in the mixture, C_N is the activity, due to nitrogen, under the photo

peak of 0.511 MeV gamma-rays, C_{Al} is the activity due to aluminium, under photo peak of 0.84 MeV gamma-rays and K is the activation constant. Following the above procedure, the activation constant "K" was separately determined using 99.9% pure sodium nitrate in which nitrogen content was known. Experimentally determined average value of K was 1.22.

2.2. Estimation of oxygen :

The amount of oxygen in each sample was determined by using sodium as a monitoring element. Mixture of test sample and sodium (in the form of sodium chloride), was irradiated for 30 seconds and the induced gamma-ray activities due to ^{16}N and ^{20}F were measured for 30 seconds. The details of the nuclear reactions of oxygen and sodium with 14 MeV neutrons considered in this work are as follows

$$^{16}O\ (n, p)^{16}N\ ;\ \sigma = 42\ mb\ ;\ T_{1/2} = 7.3 \text{ sec and } E_\gamma = 6.13 \text{ MeV (69\%)}$$
$$\text{and } 7.11 \text{ MeV (50\%)} \quad (4)$$

$$^{23}Na\ (n, \alpha)^{20}F,\ \sigma = 222\ mb\ ;\ T_{1/2} = 11 \text{ sec}\ ;\ E_\gamma = 1.63 \text{ MeV (100\%)}. \quad (5)$$

The following formula was used for the estimation of oxygen in each sample,

$$W_O / W_{Na} = K_1 C_O / C_{Na} \quad (6)$$

where W_O is the weight of oxygen in the test sample, W_{Na} is the weight of sodium in the mixture, C_O is the activity due to oxygen under the photo peak of 6.13 MeV, C_{Na} is the activity due to sodium under the photo peak of 1.63 MeV and K_1 is the activation constant. The average value of K_1 was found to be 1.78 which was separately determined using $NaNO_3$ as a standard. The concentration of oxygen in each sample was determined by following the procedure as discussed for the nitrogen analysis.

2.3. Determination of chlorine and hence ammonium perchlorate :

The amount of chlorine in the sample was estimated using manganese (in form of manganese dioxide) as a monitor. The nuclear reactions which were considered in this work are as follows :

$$^{37}Cl(n, p)\ ^{37}S\ ;\ \sigma = 40\ mb\ ;\ T_{1/2} = 5.06 \text{ min and } E_\gamma = 3.09 \text{ MeV} \quad (7)$$

$$^{55}Mn\ (n, \alpha)\ ^{52}V\ ;\ \sigma = 52.5\ mb\ ;\ T_{1/2} = 3.76 \text{ min and } E_\gamma = 1.45 \text{ MeV} \quad (8)$$

The mixture of the test sample and manganese dioxide was irradiated for 5 minutes and the gamma-ray activities due to ^{37}S and ^{52}V were recorded. The following formula was used to estimate chlorine in the sample

$$W_{Cl} / W_{Mn} = K_2 C_{Cl} / C_{Mn} \quad (9)$$

W_{Cl} is the weight of chlorine in the test sample, W_{Mn} is the weight of manganese

in the mixture, C_{Cl} is the activity due to chlorine under photopeak of 3.09 MeV, ^{C}Mn is the activity due to manganese, under photo peak of 1.45 MeV. The activation constant K_s was determined using KCl as a standard. The total amount of ^{37}Cl and abundances of ^{35}Cl and ^{37}Cl in natural chlorine. From the amount of total chlorine in the test sample, the amount of ammonium perchlorate in the propellant was estimated.

2.4. Decomposition of the propellant :

A triple base propellant containing nitro-cellulose, nitroglycerine and picrite as major ingredients was used as a representative sample to study weight loss of nitrogen in a propellant at 71.6°C. Five samples of the propellant each of weight 300 mg were separately heated into a constant temperature bath at 71.6°C. The period of heating was varied from sample to sample, covering a range from 30 minutes to 150 minutes, in step of 30 minutes. Concentrations of nitrogen in each sample before and after heating were estimated by 14 MeV neutron activation analysis technique. Weight method was used to measure total loss in weight of the sample due to its decomposition on heating. Results of this study are shown in Figure 1.

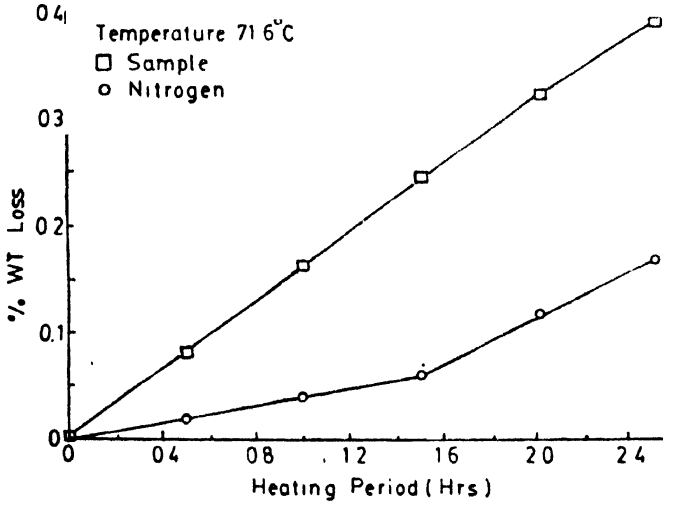

Figure 1. Weight loss of (i) nitrogen in a propellant sample and (ii) of the sample, with period of heating at 71.6 °C.

3. Results and discussions

Table 1 gives details of the experimentally determined concentrations of nitrogen and oxygen in different types of propellants, ammonium perchlorate and conventional high explosives. These values were compared with the corresponding theoretically calculated values using chemical formula (Olsen and Greene 1945) in

case explosives or by considering the compositions in case of propellants. In majority of cases, the experimental values are in good agreement with those obtained theoretically. However, in some cases the deviations of experimental values from theoretically calculated values have been observed which may be due to certain impurities present in the test sample. Application of this technique can also be extended to estimate contents of other elements which may be useful to judge level of purity of an explosive or propellant sample. With additional experimental setup it may be possible to identify hidden explosives (Urbanski 1984) in places of public interest.

The experimental and calculated values of chlorine and hence ammonium perchlorate are listed in Table 2. It is seen that in most of the cases, the amount

Table 2. Concentrations of chlorine and ammonium perchlorate in some composites and CMDB propellants.

Propellants/ composites	Chlorine	Chlorine	Ammonium perchlorate
Code No.	Calculated %	Experimental %	Experimental
CP-1	22.6	20.0	66.30
CP-2	20.2	22.0	72.93
CP-3	20.6	22.0	73.4
CP-4	1.8	4.0	13.3
CP-5	24.4	26.0	86.3
CP-6	6.2	5.0	16.61

of ammonium perchlorate determined experimentally, is close to the values estimated on the basis of the processes adopted for making propellant grains. In a few cases this agreement is not good, indicating thereby that the propellant grains formed are not having desired compositions. The errors might be creeping in during the manufacturing process.

On the basis of the oxygen to nitrogen ratio, most of the samples were found to fit for practical application. We have analysed several other samples in which percentage of oxygen was found to be much lower than desired.

For a triple base propellant, Figure 1 shows percentage weight loss (i) of nitrogen in the sample and (ii) of the sample, with period of heating at 71.6°C. The rate of weight loss for the sample is almost linear with the period of heating. However, the curve for the nitrogen has two different rates for weight loss in a period of 150 minutes, indicating that nitrogen must be evolving from two different chemical groups of the sample. Loss of weight of oxygen in the sample can also be estimated following similar experimental approach.

Precision with which elemental concentration can be estimated depends on several factors such as matrix of the sample, uniformity of irradiation, detector parameters, isotopic abundance, etc. For the samples used in the present work, the accuracy of nitrogen estimation is around 50 PPM whereas for oxygen and chlorine it is better than 80 PPM.

4. Conclusion

Concentrations of nitrogen, oxygen and chlorine (hence ammonium perchlorate) in explosives and propellants can be estimated quantitatively using 14 MeV neutron activation analysis technique which is nondestructive, accurate and less time-consuming. The technique is particularly suitable for explosives as the quantity required for the analysis is small, thereby making it safe and nonhazardous as compared to other conventional methods.

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